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(54) Bacterial leaching of minerals.

(57) In the leaching of minerals, especially ferrous sulphide ores, it is known that certain bacteria, especially Thiobacillus, can oxidise the ore to ferric sulphate. The ferric ions can convert other metal species to the soluble state.

The invention proposes supplying oxygen to these bacteria by supplying it in combined form, e.g. as hydrogen peroxide, a per compound or a peroxygen addition compound.

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TITLE MODIFIED
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LEACHING OF MINERALS

The present invention relates to methods of leaching minerals in order to extract metal values in a soluble state. More particularly the invention relates to the mirco-biological leaching of these metallic ores.

It is known that sulphide ores frequently contain ferrous iron, either as such or in combination with other metals forming more complex sulphides. It is also known that certain varieties of bacteria, chiefly those known as Thiobacilli (including Ferrobacilli) and more specifically Thiobacillus ferro-oxidans and Thiobacillus thio-oxidans, have the ability to oxidise the sulphide and ferrous ions to sulphate and ferric ions, which, in aqueous solution, are known to have the ability to leach other minerals, such as ores of uranium (and other actinides), cadmium, cobalt, tin, titanium, copper, nickel, zinc and molybdenum for example. Thus, valuable metals are leached, probably as soluble sulphate species. Although these bacteria occur naturally in association with mineral ores they are not generally very resistant to acid leaching solutions so that the natural leaching effect is limited. Various measures have been proposed to enhance the effect.

A review of the techniques used generally in this art was published by O.H. Tuovinen et al in International Metallurgical Reviews 1974 Vol 19 No. 179.

Since these bacteria are aerobic an adequate supply of oxygen is necessary to maintain them active. The leach liquors have been aerated even if only by being used in such

a way that there is an exposure to the atmosphere.

It is an object of the present invention to provide means for improving the effectiveness of this micro-biological leaching technique.

According to the present invention, in the bacterial leaching of ores, oxygen is supplied to the bacteria in available combined form.

The term "leaching of ores" should be construed widely enough to encompass the bacterial treatment of ores in situ, mined ores, dressed ores, partly leached ores, waste, slimes and leach liquors for example.

The available combined oxygen may be supplied in solution, e.g. in the form of hydrogen peroxide, or in a solid form using a percompound such as peroxide, perdi-sulphate, hydrogen peroxide addition compounds such as percarbonate, or the like. The choice of a solid or liquid source for the combined oxygen will depend upon the precise leaching operation being conducted.

As explained in the said review article, the action of acid resistant strains of Thiobacillus ferro-oxidans in dilute sulphuric acid is to oxidise ferrous sulphate to ferric sulphate and it is known that ferric sulphate will react with, for example uranium dioxide, in order to produce uranyl sulphate and ferrous sulphate. Thiobacillus ferro-oxidans and also to some extent Thiobacillus sulpho-oxidans are capable of oxidising sulphides and possibly even elemental sulphur to give sulphate ions and these sulphate ions may, if the acidity conditions are right, directly leach the wanted ore or, if they are associated with iron sulphides originally, they may give rise to ferric sulphate which will leach the ores as described above.

Desirably, therefore, the ores to be leached also contain iron compounds and specifically iron sulphides. It should be mentioned that in the event that the ore does not contain any iron compounds it may be desirable to add

them, but such a condition is unlikely to be met in practice. Finally, if the ore does not contain any natural sulphides at all, these may be added to promote the leaching effect or a chemical equivalent can be achieved by adding natural sulphur. It should be explained finally that although the application of the invention to the leaching of iron ores in order to obtain iron values is not excluded, such an operation is unlikely to prove commercially viable. The invention will therefore normally be directed to the leaching of more valuable minerals. However the invention may be applied to oxidising ferrous liquors to ferric, for example in order to use them as ferric leach liquors.

We prefer to operate using Thiobacillus ferro-oxidans which is essentially characterised by its ability to oxidise ferrous iron in acidic solutions. We prefer to use selected acid-resistant strains which can operate down to pH 1.0 for exaple the Beck strain (ATCC 13,598: NCIB 8,451), the Lundgren strain (ATCC 13,661); the Sutton strain (ATCC 13,728); the Trussel strain (ATCC 19,859; NCIB 9,490); and a strain deposited in the American Type Culture Collection, Washington D.C., under the number ATCC 12,241. Another suitable strain is one found in Mount Lywll, Tasmania and identified by D Lacey and F Lawson in the Journal "Biotechnology and Bio-Engineering" 1970 Vol 12 Pages 29-50.

It is also desirable to supply nutrients for the bacteria and suitable nutrients may include, in suitable predetermined quantities, sources of nitrogen, phosphorus and carbon dioxide. Typically suitable nutrient media are (i) that of Silverman and Lundgren known in the art as 9k medium; and (ii) a modification of the 9k medium where the ammonium sulphate concentration is doubled and the phosphate concentration is reduced to 20% of the standard figure.

Hitherto the leaching procedure has been carried out in situ or upon mined ore after a suitable crushing or

dressing operation and aeration of the leach liquor to add oxygen has provided the addition of carbon dioxide, see for example US Patent 3 607 235. In practising the present invention the use of aeration is not precluded in order to effect the addition of carbon dioxide. However carbon dioxide can be provided by other means.

It is known that these bacteria are more efficient in their leaching operation at elevated temperatures and this suggests that the leaching of this invention should be applied to extracted ore under controlled temperature conditions normally at least 20°C up to 70°C, the higher end of the range, i.e. 50 to 70°C, being used in conjunction with strains of bacteria that are or have been conditioned to be tolerant of such temperatures. On the other hand in situ leaching of the ore body before it is removed from the mine may be cheaper (although it may be slower) and in suitable circumstances may therefore be preferred. Suitable selection of the bacteria and leach liquor having regard to the conditions of leaching, e.g. metals present, temperature and pH, will improve the yield.

We have demonstrated satisfactorily that the oxygen requirements of aerobic bacteria can be provided by hydrogen peroxide and other peroxidic species, but it is not clear from our studies whether the bacteria utilise the peroxidic species directly or whether they uptake oxygen from the water. Clearly the use of peroxidic species, including those which are slow to dissolve in water, can supply a level of oxygen in the water, both combined and dissolved, which is greater than can be maintained by the simple injection of air as by sparging, particularly having regard to the low solubility of oxygen at low temperatures. The precise mechanism of utilisation of the oxygen by the bacteria is however clearly not important.

It will be understood that the use of dissolved peroxygen species can permit the supply of available oxygen

much more readily than the use of an air sparge or the like since it can be supplied closer to the point of utilisation. Thus for example hydrogen peroxide can be supplied adjacent to a natural ore body. In the case of the leaching of heaps of dressed ore, it is normally found that the aeration introduces so little oxygen that this is only supplied to the bacteria close to the surface of the heap, with the result that the bottom of the heap may even contain sulphate-reducing bacteria. This extremely inefficient or undesirable situation can be avoided by the use of the present invention. Particularly in the case of large heaps direct injection of hydrogen peroxide into the heaps may be desirable. The use of solid peroxygen species is also of general applicability to the leaching of heaps of ore since the solid species can be incorporated in the heaps as they are built.

Since hydrogen peroxide can also function as a bactericide and indeed has been known for many years as a general disinfectant, it is therefore desirable to supply it in diluted form in order that it should not kill the bacteria it is supposed to supply with oxygen for their growth. A suitably safe level is diluted in water to approximately 100 milligrams of hydrogen peroxide per litre of water.

The result of a leaching operation in accordance with the present invention will be a solution containing sulphate ion and the ions of the metal values that are of interest. This dilute solution is then worked up in known fashion.

As explained, the bacteria occur naturally in association with mineral ores and known techniques permit the selection of strains of bacteria which are tolerant to acid and tolerant to the metals present in the ores. However, for our experiments we did not use specially tolerant strains of bacteria and under the conditions used we found no inhibiting effects. If we had used specially

selected strains of bacteria, it would have been possible to operate at lower pH values and at higher metal ion concentrations.

Two series of experiments were carried out, the first using Thiobacillus ferro-oxidans, identified as strain TF, and the second using a Thiobacillus sp. identified as TH1, which is capable of growth on mineral sulphides such as pyrites.

The bacteria TF was grown in a medium comprising, in grams per litre:-

K_2HPO_4	0.4
$(NH_4)_2SO_4$	0.4
$MgSO_4.7H_2O$	0.4
$FeSO_4\ 7H_2O$	27.8

The pH was adjusted to 1.5 using sulphuric acid. The cultures (100ml) were incubated in 250ml conical flasks at 30°C and 140rev/min in an orbital shaker. The growth of the bacteria followed the standard growth curve with a lag phase initially of up to 14 days. The progress of the growth was followed by a standard form of analysis for both ferric and ferrous iron and better than 95% conversion to ferric iron was achieved. In order to provide stock cultures, 2% by volume inocula were taken when at least 95% of the iron had been oxidized. After serial culture in this way the lag phase fell to approximately 1 day.

The oxygen in available combined form was used in the experiments in the form of dilute hydrogen peroxide and the quantities given herein are quoted as 100% H_2O_2. It is known that hydrogen peroxide oxidises ferrous iron to ferric iron.

In order to check the effect of hydrogen peroxide on the bacteria, hydrogen peroxide equivalent to approximately 25% conversion to ferric iron was added to the growing cultures at different points in the growth curve, giving a concentration of 100mg/l hydrogen peroxide. No inhibition effect was detected, as the growth curves

maintained the same shape and the cultures could be used as inocula. The normal content of oxygen in a leach liquor is of the order of 5-7mg/l and the initial object of the experiments was to double this oxygen content by adding approximately 10mg/l oxygen as hydrogen peroxide, i.e. 10% of the above addition.

A further experiment was carried out using cultures after full conversion to ferric iron. To separate samples of these cultures were added 10, 100 and 1000mg/l of hydrogen peroxide. The decomposition of the hydrogen peroxide was monitored and was shown to be approximately first order, thus indicating that substantially complete conversion to ferric iron had taken place. The cultures were used as inocula after standing for 24 hours and it was found that the culture to which 1000mg/l of hydrogen peroxide had been added showed evidence of distruction of some, but not all, of the bacteria. Thus for these bacteria under these conditions, the toxic level of hydrogen peroxide was established.

In the first series of experiments using the bacterium TF attempts were made to extract the uranium content of a uranium ore from Buffelsfontein in South Africa. This ore contains 250mg uranium per kg and was made up into a pulp or paste at 10gms of ore per 100ml, corresponding to an approximate uranium concentration of 25mg/l uranium. In addition the culture medium contained potassium, ammonium, and magnesium as above described but no added iron as the iron content of the ore was sufficient to obtain leaching. Before the experiments began the bacteria strain was checked for tolerance to uranium and it was found that it would withstand concentrations of the order of 700mg/l uranium, well in excess of any figures likely to be obtained. Throughout the experiments the initial culture medium was made up and was then inoculated at time t=0 with 2% by volume of a growing culture; 10ml samples were withdrawn at intervals

and analysed. It will be appreciated that it is very difficult to ensure that the samples withdrawn are homogeneous and especially towards the end of an experiment the amount remaining in the flask was very small. Nevertheless, in spite of these difficulties inherent in the techniques that have to be used and the inherent varability in microbiological procedures, a clear effect was demonstrated.

It will be appreciated that, as in the experiments to test the tolerance of the bacteria to hydrogen peroxide, the addition of hydrogen peroxide to the ore pulp will result in oxidation of ferrous iron to ferric iron. It will also be appreciated that ferric iron reacts with the uranium in the ore in order to convert the insoluble quadravalent uranium into soluble hexavalent uranium, with a corresponding reduction of the ferric iron to ferrous iron. In order to avoid the errors that would be involved in using an inoculum containing ferric iron the inoculum was centrifuged and washed three times to remove iron. A preliminary experiment was done in which no centrifuge washing was carried out but iron was deliberately added to correspond to the iron contained with the bacteria and it was found that the washing procedure introduced no harmful effect. In all cases parallel experiments were run, being started and stopped together in order to reduce the variables.

Experiment 1

The object of this experiment was to demonstrate the ability of the bacteria to leach uranium under aerobic conditions.

Table 1 represents the results of two experiments 1a and 1b. In experiment 1a no bacteria were added, whilst in experiment 1b the bacteria were added as above described. The gas space above the pulp in the flask contained air and its oxygen content was slowly absorbed by the pulp in order to give slow oxidation of ferrous iron to, ferric iron and

consequent leaching of the uranium. Under these conditions, the efficiency of the bacteria in leaching uranium from its ore is clearly demonstrated, at being remembered that the samples contain 25mg/l uranium.

Table 1

Time (hours)	Concentrations mg/l					
	Uranium		Ferrous iron		Ferric iron	
	a	b	a	b	a	b
0	<3	<3	17	15	1	4
23	3	5	54	0	7	9
65	5	12	71	6	6	32
143	3	17	80	48	0	346
233	4	22	97	88	0	893

Experiment 2.

The object of this experiment was to demonstrate the ineffectiveness of hydrogen peroxide to leach uranium from the ore, in the absence of bacteria, and to simulate anaerobic conditions.

In experiment 2, the results of which are shown in Table 2, the procedure in experiment 1 was followed except that at the start of the experiments, 14mg/l hydrogen peroxide were added to the pulp, this being approximately twice the stoichiometric amount of hydrogen peroxide required to oxidise all the uranium. That this oxidation did not in fact take place is clearly shown from the table, the reason being that the ferrous iron present in the pulp caused the immediate decomposition of the hydrogen peroxide. In experiment 2a no bacteria were present whereas in experiment 2b the bacteria were added as above described. At time 168 hours it was discovered that the method of analysis used for uranium was suspect and therefore the method was changed to a more accurate method. The results

shown in Table 1 and 2 may therefore not be comparable with each other, although in both cases the results of experiments a and b are comparable. Table 2 clearly demonstrates that the addition of hydrogen peroxide does not increase the leaching of uranium from the ore in the absence of bacteria.

The experiments of Table 1, since they were conducted with air above the culture, correspond to the fully aerated leach liquors that are desirable in theory but unobtainable in practice. In order to simulate practical leaching conditions, in experiment 2, the air space above the culture in the flask was purged three times with nitrogen and then the flask was sealed with a nitrogen atmosphere above the culture. It should be noted that this procedure does not remove the air dissolved in the culture and no continuous purge of nitrogen was used; the conditions therefore closely simulate heap leaching.

The results of experiment 2b clearly demonstrate that hydrogen peroxide can be used to replace the air and enable the bacteria to grow and oxidise the ferrous iron with consequent leaching of the uranium.

In order to check whether a source of carbon was necessary in order to enable the bacteria to grow, at time 265 hours 10ml of carbon dioxide was added to the gas phase above the culture. It will be seen that no significant change occurred.

Table 2

Time (hours)	Concentrations mg/l					
	Uranium		Ferrous iron		Ferric iron	
	a	b	a	b	a	b
0	<3	<3	27	2	3	2
24	<3	4	40	0	4	6
96	<3	6	80	1	2	13
168	-	-	89	5	3	-
264	1.3	9	97	37	4	14
360	1.3	12	89	76	1	14
432	1.0	13	89	80	3	35

For the second series of experiments Thiobacillus sp. identified as TH1 was used. For further information on this Thiobacillus see Norris et al FEMS Microbiology Letters 4 (1978) 143-146. This bacteria was maintained by serial transfer in a pyrites medium. The culture medium contain potassium, ammonium and magnesium as for the bacteria TF but in place of the iron the culture medium contained 10g/l of pyrites. The samples of pyrites used came from Tharsis in Spain and was ground to less than 200 mesh. The pH of this culture medium was adjusted to 2.0.

It should be pointed out that this bacterium appears to grow on the solid substrate and therefore the inoculum used was 2% of the suspension.

Initial checks showed that this bacterium was sufficiently tolerant to hydrogen peroxide and copper for the experiments to continue but a specially selected strain was not developed.

In the second series of the experiments, the ore chalcopyrite was used, being ground to less than 150 mesh before being used. A check using sterilised ore showed that sterilisation was unnecessary. This ore contains approximately 213g/kg copper and 273g/kg iron. The culture

medium for the experiments contained 10g/l chalcopyrites, corresponding approximately to a concentration of 2g/l copper.

Experiment 3

The object of this experiment was to demonstrate the ability of the bacteria to leach copper from the ore under aerobic conditions. Consequently the atmosphere above the culture medium was air.

The inoculum used was a suspension of the stock culture and therefore contained free iron. In experiment 3b, the pulp was inoculated with the bacteria whilst in experiment 3a, an iron-containing but bacteria-free "inoculum" was used. This experiment clearly shows in Table 3, that the bacteria can leach copper from the ore under these conditions.

Table 3

Time (hours)	Concentrations mg/l					
	Copper		Ferrous iron		Ferric iron	
	a	b	a	b	a	b
0	22	18	66	63	127	136
44	92	88	207	168	7	22
187	136	182	256	127	8	80
279	158	236	244	56	34	281
360	170	280	-	56	44	449
450	190	320	276	117	-	649
546	175	350	256	103	29	905
618	210	380	254	85	34	1042

Experiment 4

The object of this experiment was to demonstrate the inefficiency of the bacteria in leaching copper under anaerobic conditions.

Thus in this experiment, nitrogen replaced the air

above the culture in order to simulate normal leaching conditions. In experiment 4c hydrogen peroxide was added at the start in an amount equivalent to 100mg per litre but the culture contained no bacteria, so that experiment 4a demonstrates solely the effect of hydrogen peroxide. In experiment 4b, the hydrogen peroxide was added as in experiment 4a but additionally the culture was inoculated with bacteria. The results of these experiments shown in Table 4 demonstrate the importance, by contrast with experiment 3, of the importance of oxygen to the process and by contrast between the two parts of this experiment to the activity of the bacteria in promoting leaching of the copper. Clearly this experiment also demonstrates that the presence of hydrogen peroxide promotes the activity of the bacteria under simulated leaching conditions. In Table 4 the differences in iron concentration a time of t=0 as compared with Table 3 is due to the effect of the iron contained in the inoculum, since in experiment 4b washed pyrite was used as the inoculum and no iron was added in experiment 4a.

Table 4

Time (hours)	Concentrations mg/l					
	Copper		Ferrous iron		Ferric iron	
	a	b	a	b	a	b
0	55	93	14	146	6	142
24	86	108	54	149	2	63
96	120	140	105	234	15	88
168	114	174	127	315	7	37
264	126	186	139	373	7	61
360	108	192	132	478	7	10
432	130	210	154	412	0	68

Experiment 5

The object of this experiment was to determine whether addition of the hydrogen peroxide in stages would be beneficial, under anaerobic conditions.

In this experiment, the results of which are given in Table 5, the ore was again chalcopyrites, but the hydrogen peroxide was added in 0.2cc amounts (each of concentration 10g/l hydrogen peroxide) four times in every working day. The first addition of hydrogen peroxide was made at time t=0 which was after the conclusion of a lag phase of 18 hours. In experiment 5a no hydrogen peroxide was used, but the pulp was inoculated with the standard inoculum of bacteria on pyrites. In experiment 5b the hydrogen peroxide was added to the pulp to which the bacteria inoculum had been added. It will be observed from the paper by Norris et al referred to above, that he believed it to be necessary to add a yeast extract to promote the growth of the bacillium TH1 and therefore in this experiment such yeast extract (1 ml of extract containing 20g/l yeast extract) was added at time t=95.

The results in Table 5 indicate that there is difficulty in measuring the iron content under these conditions and we believe that this is either due to a yeast/iron complex which may be a solid and so is removed before the analysis is conducted or alternatively that, since the bacteria require iron for their metabolism, under low concentrations of iron they may produce iron complexing agents which contribute to the difficulties of analysis. However, Table 5 shows quite clearly the effectiveness of the addition of hydrogen peroxide in substantially doubling the total extraction of copper from the ore sample.

Table 5

Time (hours)	Concentrations mg/l					
	Copper		Ferrous iron		Ferric iron	
	a	b	a	b	a	b
0	72	73	152	145	12	16
24	80	104	179	64	0	1
48	84	132	195	70	0	1
94	88	156	197	73	6	10
142	90	180	96	81	2	6
190	98	186	46	98	53	14
262	116	200	34	114	61	52

Although the invention has only been demonstrated herein in respect of two ores, it will be appreciated that it can be applied to any leaching operating using aerobic bacteria, in itself a known technique.

Claims

1. A process for the bacterial leaching of ores to extracting metal values therefrom, wherein oxygen is supplied to the bacteria in available combined form.

2. A process as claimed in claim 1 wherein the available combined oxygen is supplied in solution form.

3. A process as claimed in claim 2 wherein the available combined oxygen is supplied as hydrogen peroxide solution.

4. A process as claimed in claim 1 wherein the available combined oxygen is supplied in solid form.

5. A process as claimed in claim 4, wherein the available combined oxygen, is supplied as a percompound.

6. A process as claimed in claim 4 wherein the available combined oxygen is supplied as a peroxide addition compound.

7. A process as claimed in any of the preceding claims, wherein the leaching is effected in the presence of compounds of iron and sulphur and under acid conditions.

8. A process as claimed in claim 7 wherein the sulphur is present as sulphate and the bacteria is Thiobacillus ferro-oxidans.

9. A process as claimed in claim 8 wherein nitrogen, phosphorous and carbon dioxide are supplied as nutrients for the bacteria.

10. A process as claimed in claim 7, wherein the sulphur is present as sulphide and the bacteria is Thiobacillus sp.

11. A process as claimed in claim 10 wherein nitrogen, phosphorous and yeast are supplied as nutrients for the bacteria.

12. A process as claimed in any preceding claim wherein the leaching is carried out at temperature in the range of from 20°C to 70°C.

European Patent Office

EUROPEAN SEARCH REPORT

0004431
Application number
EP 79 30 0373

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 3 679 397 (L.T. O'CONNOR)	
A	US - A - 3 266 889 (D.W. DUNCAN)	
A	FR - A - 2 169 263 (CENTRE DE RECHERCHES MINERALES, MINISTERE DES RICHESSES NATURELLES DU QUEBEC)	
A	FR - A - 2 278 631 (GENERAL MINING AND FINANCE CORPORATION LTD.)	
A	US - A - 3 268 288 (M.B. GOREN)	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 22 B 3/00
C 12 D 13/00

TECHNICAL FIELDS SEARCHED (Int.Cl.³)

C 22 B
C 12 D

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	21-06-1979	JACOBS

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